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PROGRESS REPORT ON RESEARCH INTO CHEMICAL STRUCTURE/BONDING DEC--ETC(U)  
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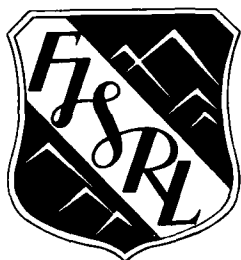
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**FRANK J. SEILER RESEARCH LABORATORY**

**FJSRL TECHNICAL REPORT 80-0026**

**DECEMBER 1980**

**PROGRESS REPORT ON RESEARCH  
INTO CHEMICAL STRUCTURE/BONDING  
DECOMPOSITION RELATIONSHIPS FOR  
ENERGETIC MATERIALS**

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**PROJECT 2303**

**AIR FORCE SYSTEMS COMMAND**

**UNITED STATES AIR FORCE**

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FJSRL-TR-80-0026


This document was prepared by the Energetic Materials Division, Directorate of Chemical Sciences, Frank J. Seiler Research Laboratory, United States Air Force Academy, Colorado. The research was conducted under Project Oerk Unit Number 2303-F3-05, "Chemical Structure/Bonding Decomposition Relationship". Captain R. Cameron Dorey, III was the Project Scientist in charge of the work.

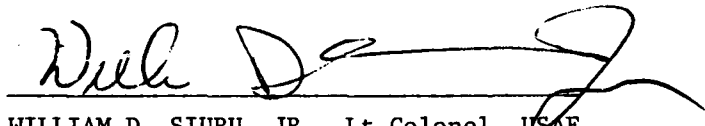
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PROGRESS REPORT ON RESEARCH INTO CHEMICAL STRUCTURE/BONDING  
DECOMPOSITION RELATIONSHIPS FOR ENERGETIC MATERIALS

By

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DECEMBER 1980

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# ABSTRACT

Photochemical and thermal decomposition of nitroaromatic compounds and nitramines has been studied by electron paramagnetic resonance spectroscopy. Radicals are obtained from both types of compounds, indicating a mechanism for their decomposition. Photolysis of nitroaromatics in ethers results in a radical produced with solvent interaction, whereas photolysis in other solvents and all photolysis of nitramine produces a radical formed by cleavage of a nitro group from the parent compound. Thermal decomposition studies have been undertaken using binary mixtures of compounds in the search for an inert high-temperature solvent.

## PREFACE

The work described in this report was performed in Work Unit 2303-F3-05 in the Frank J. Seiler Research Laboratory, USAF Academy, Colorado. Part of the work was performed under Contract ATL-0-092 from the High Explosives Research and Development Laboratory, Air Force Armament Testing Laboratory, Eglin AFB, Florida, under the supervision of Thomas Floyd.



## TABLE OF CONTENTS

	<u>PAGE</u>
ABSTRACT . . . . .	i
PREFACE . . . . .	ii
FIGURES . . . . .	iv
INTRODUCTION . . . . .	1
EXPERIMENTAL . . . . .	4
DISCUSSION . . . . .	5
PHOTOCHEMICAL STUDIES. . . . .	5
THERMOCHEMICAL STUDIES . . . . .	18
CONCLUSIONS . . . . .	24
PLANS FOR FUTURE STUDY . . . . .	26
LIST OF ABBREVIATIONS . . . . .	27
REFERENCES . . . . .	28

## FIGURES

1. Observed and simulated EPR spectra of TNT in dioxane under ultraviolet irradiation.
2. Observed and simulated EPR spectra of  $\text{PiCl}$  in dioxane under ultraviolet irradiation.
3. Observed and simulated EPR spectra of TNB in dioxane under ultraviolet irradiation.
4. Time-dependent EPR spectra of TNT in dioxane under ultraviolet irradiation.
5. EPR spectra of TNT under various conditions.
6. Observed EPR spectra of RDX and HMX.
7. Observed and simulated EPR spectra of the early HMX radical under ultraviolet irradiation.
8. Observed and simulated EPR spectra of the early RDX radical under ultraviolet irradiation.
9. Observed and simulated EPR spectra of the late photolytic (lamp extinguished) HMX radical.
10. Observed and simulated EPR spectra of the late photolytic (lamp extinguished) RDX radical.
11. Mechanisms for TNT thermal decomposition step currently being evaluated theoretically.
12. Theoretical energy diagram for intramolecular hydrogen transfer mechanism for TNT thermal decomposition.

## INTRODUCTION

Our work in FJSRL Work Unit 2303-F3-05 has been directed toward finding the mechanisms of thermal decomposition of energetic materials (explosives, propellants, etc.). This is being done in order to determine the chemical characteristics of the materials which could lead to an increase (or loss) of thermal stability. When energetic materials currently in the inventory are subjected to high temperatures, they may either degrade to inert substances or (less often) explode. This becomes important in two instances. First, munitions are commonly stored in warehouses without any environmental control for long periods of time. During this time, the warehouse temperature can fluctuate greatly. Second, vehicles are now being designed to carry external ordnance at extreme speeds. Here, aerodynamic (friction) heating of the casing can lead to a rapid temperature rise of the entire ordnance.

During 1980, we concentrated on photolysis of energetic materials. We hoped to produce candidates for thermal decomposition intermediates, or at least structures simpler than those found in thermal decomposition to aid in our analysis. We felt that we could control conditions more easily and we had the opportunity to use solvents unavailable in thermal work. Also, photolysis of certain energetic materials is a problem in its own right. An example is the photolysis of trinitrotoluene (TNT)<sup>a</sup> which discolors the solid, or leads to "pink water" in manufacturing effluents<sup>1</sup>.

We have concentrated on using electron paramagnetic resonance (EPR) techniques in our work recently. In our application, EPR spectroscopy

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<sup>a</sup> Chemical abbreviations used are found at the end of this report.

yields information about radical species in samples, species with unpaired electrons because of the fragmentation of a molecule or addition or extraction of an electron to a molecule. By their very nature, these species are unstable and cannot usually be isolated. They often occur as intermediates in chemical reactions, and we have found radicals to be strongly involved in decomposition of many energetic materials.

The phenomenon behind EPR spectroscopy is the absorption of microwave energy by a free electron, or one unpaired but associated with an atom, ion, molecule, or radical. The electron will absorb microwave energy when a magnetic field is applied such that the combination of microwave radiation and magnetic field provides enough energy to the electron to allow it to change between two spin states (vis. a vis. NMR). Since the absorption is small, measurements are normally taken of the derivative of the absorption at a point. Usually in an EPR experiment, the microwave radiation is held at a constant frequency and the magnetic field is varied, so that the hyperfine splittings (vide infra) in the absorption pattern of a radical is given in terms of magnetic field strength (Gauss).

EPR gives two types of information about a radical, first the spectroscopic splitting factor,  $g$ , which is indicative of the shielding of the unpaired electron from the external magnetic field applied by the instrument. For organic molecules, this number is very close to 2.005, and is not very useful for our work. The important information in EPR for organic radical structure identification is the hyperfine splitting by nuclei in the radical of the microwave absorption of the unpaired electron. The number of lines the electron absorption line is split into, the magnitude of the splittings in Gauss, and the intensities of the lines tell what atoms are contained in the radical. Fortunately, carbon and oxygen do not interact

with the unpaired electron, so that the only splittings we observe in our studies are of hydrogen and nitrogen. Chlorine and deuterium do interact with the unpaired electron, but only very weakly, and are also not observed here.

EPR is unique in that short-lived radical intermediates can be observed and identified, but it has a disadvantage, namely many types of samples and solvents are unusable. Very polar materials such as water and acetonitrile have a high enough dielectric constant that they absorb too much microwave radiation (they are "lossy") and make it impossible under normal conditions to operate the spectrometer. Special techniques and sample cells make some measurements possible using these substances, but a high price is paid in sensitivity of the measurement.

We have used EPR not only for the identification of organic radicals, from a variety of substances, but also for measurement of the rate of formation of radicals derived from TNT. Either spectra can be taken and the intensity of a line can be measured manually, or the spectrometer can be set to continuously measure the absorption at a single field strength. This mode of operation enables us to perform studies on the molecularity of TNT decomposition. Whether the radical-producing step is unimolecular or bimolecular can be easily shown by diluting the sample of TNT with an inert solvent and observing the change in reaction rate with concentration. The rate of a unimolecular reaction varies linearly with the reactant concentration, while the rate of a bimolecular reaction varies with the square of the reactant concentration.

Finally, we have been employing molecular orbital (MO) calculations to predict energy profiles for decomposition mechanisms for TNT. For a

specific reaction scheme we can calculate an internal energy profile through the course of the reaction. This enables us to estimate the feasibility of different mechanisms according to their probable activation energies.

#### EXPERIMENTAL

For the EPR work, we used a Varian E-109 EPR Spectrometer in the first derivative mode operating at approximately 9GHz. The E-272B field/frequency lock accessory was employed to record all spectra relative to the sharp line spectrum of DPPH. A TE<sub>102</sub> rectangular cavity was used, with a louvered grid for light transmission in the photochemical studies and a solid front wall in temperature studies. The samples were housed in standard quartz EPR sample tubes inside a S-821 quartz dewar assembly (J. F. Scanlon Co.) through which dry nitrogen was passed.

In photochemical studies, an Oriel 1000W Hg-Xe high pressure lamp was used with its corresponding power supply. Unfiltered light from the lamp was columnated through the grid on the EPR cavity. A Varian variable temperature controller was used to thermostat a 20 SCFH nitrogen stream through the dewar assembly to  $25 \pm 0.5^{\circ}\text{C}$ . A Hewlett-Packard 2845M frequency counter was used to obtain accurate  $g$ -values for the radical spectra. All solutions for photolysis were 0.1M of sample in dioxane, unless another solvent was used or the compounds were not this soluble, in which case saturated solutions were used.

Temperature regulation in thermal studies was accomplished with a homemade regulator using a Leeds & Northrup Electromax III Controller and Type K thermocouple (alumel-chromel). Heating of the nitrogen stream was accomplished by a Scanlon S-838 heater housed inside a S-836 dewar, connected to the dewar inside the cavity. Approximately 2 minutes were

required to heat the sample to 200°C, with temperature stability of  $\pm 0.2^\circ\text{C}$  within ten minutes.

All commercially available chemicals were reagent grade and solids were recrystallized twice before using standard methods if required. TNT,  $\text{d}_3$ -TNT, TNB and  $\text{PiCl}$  were prepared in this laboratory using previously reported procedures<sup>2,3,4</sup>. RDX and HMX were obtained from Thomas Floyd of AFATL, Eglin AFB, Florida. Dioxane was purged of peroxides by passing it over an activated silica column, and was then stored under nitrogen.

Computer simulations of radical spectra were performed on a Digital Equipment Corporation PDP 11-45 minicomputer using a FORTRAN program donated by Ira Goldberg of Rockwell International. Molecular orbital calculations were done on a Digital Equipment Corporation VAX-780 minicomputer using the MNDO and MINDO/3 semiempirical programs developed by M. J. S. Dewar<sup>5,6</sup>.

## DISCUSSION

### Photochemical Studies

We photolyzed in dioxane all commercially available nitro-substituted toluenes and benzenes, and TNT, TNB,  $\text{PiCl}$ , TNBC, and TCTNB. A solvent was used since the compounds were all aromatic and thus highly absorbing in the ultraviolet, and a majority were solids at room temperature. Dioxane, a cyclic diether, was chosen as the primary solvent because of its low absorbance of ultraviolet and microwave radiation and satisfactory solvation of most of the compounds studied. We also hoped that it would be relatively inert in our application.

Table 1 gives the results of our survey, showing  $g$ -values for all of the radicals observed and proposed assignments of the hyperfine splitting by the various atoms in gauss. All chemical names without a solvent indicated

TABLE I. EPR Parameters for Photolysis of Nitroaromatic Compounds.

Compound <sup>a</sup>	R <sup>b</sup>	Hyperfine Splittings (Gauss)									
		a <sub>H(R)</sub> <sup>c</sup>	a <sub>H(o)</sub>	a <sub>H(m)</sub>	a <sub>H(p)</sub>	a <sub>H(a)</sub>	a <sub>N(R)</sub>	a <sub>N(o)</sub>	a <sub>N(m)</sub>	a <sub>N(p)</sub>	g
TNT	CH <sub>3</sub>	3.20	-	3.20	-	-	-	0	-	14.6	2.0050
TNT(glyme)	CH <sub>3</sub>	3.17	-	3.17	-	-	-	0	-	14.2	2.0045
TNT(diglyme)	CH <sub>3</sub>	3.19	-	3.19	-	-	-	0	-	14.21	2.0050
TNT(Et <sub>2</sub> O) <sup>1</sup>	CH <sub>3</sub>	2.28	-	2.28	-	2.28	-	0	-	15.41	2.0051
TNT(Et <sub>2</sub> O) <sup>2</sup>	CH <sub>3</sub>	3.18	-	3.18	-	-	-	0	-	3.18	2.0051
TNT(THF)	CH <sub>3</sub>	3.24	-	3.24	-	-	-	0	-	13.6	2.0051
TNT(oxepane) <sup>1</sup>	CH <sub>3</sub>	3.30	-	3.30	-	-	-	0	-	13.6	2.0052
TNT(oxepane) <sup>2</sup>	CH <sub>3</sub>	2.95	-	2.95	-	6.53	-	0	-	10.9	2.0059
TNT(CH <sub>3</sub> CN)	CH <sub>3</sub>	2.85	-	2.85	-	-	-	11.6	-	-	2.0062
TNT(molten)	CH <sub>3</sub>	1.63	-	1.63	-	-	-	11.5	-	-	2.0053
d <sub>3</sub> -TNT	CD <sub>3</sub>	-	-	3.00	-	-	-	0	-	14.2	2.0047
2,3-DNT	CH <sub>3</sub>	2.86	0.92	2.86	0.92	-	-	0	13.06	-	2.0048
2,4-DNT	CH <sub>3</sub>	3.30	1.13	3.30	-	-	-	0	-	15.3	2.0048
2,6-DNT	CH <sub>3</sub>	- <sup>d</sup>	-	-	-	-	-	-	-	-	2.0059
3,4-DNT	CH <sub>3</sub>	3.19	0.85, 1.06	3.19	-	-	-	-	6.23	6.23	2.0050
o-NT	CH <sub>3</sub>	- <sup>d</sup>	-	-	-	-	-	-	-	-	2.0059
m-NT	CH <sub>3</sub>	2.96	0.97	2.96	0.97	-	-	-	15.95	-	2.0050
p-NT	CH <sub>3</sub>	3.12	1.00	3.12	-	0.32	-	-	-	16.25	2.0048
NB <sup>1</sup>	NO <sub>2</sub>	-	2.98	0.95	2.98	0.32	15.85	-	-	-	2.0045
NB <sup>2</sup>	NO <sub>2</sub>	-	2.61	7.63, 0.99	18.6	-	0	-	-	-	2.0060
NB(THF)	NO <sub>2</sub>	-	3.13	0.95	3.13	0.35 <sup>e</sup>	14.93	-	-	-	2.0053
m-DNB	NO <sub>2</sub>	-	3.02	1.02	3.02	-	14.99	-	0	-	2.0047
p-DNB	NO <sub>2</sub>	-	3.10	0.88	-	-	13.2	-	-	1.87	2.0053
sym-TNB <sup>1</sup>	NO <sub>2</sub>	-	3.09	-	3.09	-	14.1	-	0	-	2.0047

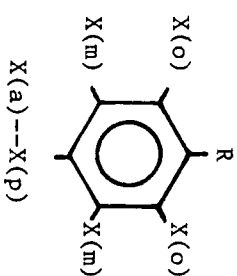


TABLE I. (Continued)

Compound <sup>a</sup>	R <sup>b</sup>	<sup>a</sup> H(R) <sup>c</sup>	<sup>a</sup> H(o)	<sup>a</sup> H(m)	<sup>a</sup> H(p)	<sup>a</sup> H(a)	<sup>a</sup> N(R)	<sup>a</sup> N(o)	<sup>a</sup> N(m)	<sup>a</sup> N(p)	g
$\delta gm$ -TNB <sup>2</sup>	NO <sub>2</sub>	-	2.60	-	2.60	9.10	9.10	-	0	-	2.0062
PICl <sup>1</sup>	Cl	-	-	-	3.13	-	-	0	-	13.6	2.0047
PICl <sup>2</sup>	Cl	-	-	-	0.60	-	-	2.86	-	9.00	
TCTNB	Cl	-	-	-	-	-	-	-	-	-	2.0058
TNBC	CH <sub>2</sub> Cl	1.58	-	3.30	-	-	-	0	-	13.4	2.0058
d <sub>2</sub> -TNBC	CD <sub>2</sub> Cl	1.60	-	3.33	-	-	-	0	-	14.6	2.0058

a. All compounds 0.1M in p-dioxane, unless another solvent identified.

b. Substituent R according to



c. Values of hyperfine splitting constant for substituent X according to above schematic.

d. Spectrum too weak to be analyzed structurally.

e. Two separate hydrogen-adduct splittings seen.

f. Spectrum strong, but could not be analyzed.

1. First free radical in time.

2. Second ("product") free radical in time.

TABLE I. (Continued)

Compound <sup>a</sup>	R <sup>b</sup>	$a_{H(R)}^c$	$a_{H(O)}$	$a_{H(m)}$	$a_{H(p)}$	$a_{H(a)}$	$a_{N(R)}$	$a_{N(O)}$	$a_{N(m)}$	$a_{N(p)}$	g
$\Delta ym-TNB^2$	NO <sub>2</sub>	-	2.60	-	2.60	9.10	9.10	-	0	-	2.0062
PiCl <sup>1</sup>	Cl	-	-	-	3.13	-	-	0	-	13.6	2.0047
PiCl <sup>2</sup>	Cl	-	-	-	0.60	-	-	2.86	-	9.00	-
TCTNB	Cl	-	-	-	-	-	-	-	-	-	2.0058
TNBC	CH <sub>2</sub> Cl	1.58	-	3.30	-	-	-	0	-	13.4	2.0058
d <sub>2</sub> -TNBC	CD <sub>2</sub> Cl	1.60	-	3.33	-	-	-	0	-	14.6	2.0058

a. All compounds 0.1M in p-dioxane, unless another solvent identified.

b. Substituent R according to

c. Values of hyperfine splitting constant for substituent X according to above schematic.

d. Spectrum too weak to be analyzed structurally.

e. Two separate hydrogen-adduct splittings seen.

f. Spectrum strong, but could not be analyzed.

1. First free radical in time.

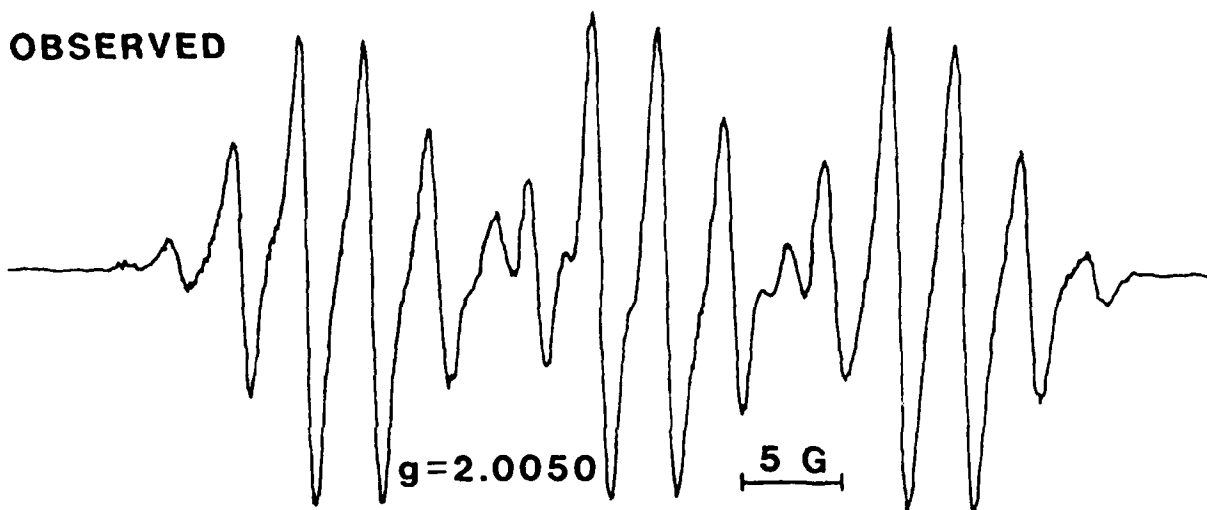
2. Second ("product") free radical in time.

represent experiments in dioxane. Where no splittings are given throughout a line, we were not able to analyze the spectrum structure. In the cases where the nitro group was adjacent only to a methyl group (o-NT and 2,6-DNT), radical production was too low to give a strong enough signal to analyze. All of the radicals formed in ether solvents were anions of the parent compounds, except where noted as one or two extra hydrogens (H(a)). The similarities between the spectral parameters suggest that the species are analogous. Extra hydrogen splittings have been noted in similar compounds in ether solvents previously, being identified as from solvent-adduct species, attached to a nitro group on the parent molecule<sup>7,8</sup>. Only one splitting due to nitrogen was found in most of the experiments in ether solvents. This has also been observed before, and is a function of cationic species in the system<sup>9</sup>.

Figures 1, 2, and 3 show the observed and simulated spectra along with the proposed structure of the radical species for TNT, Picl, and TNB respectively in dioxane. Agreement between observed and simulated spectra is good, lending credence to our structural assignments.

Figure 4 shows the time-dependent spectra observed in TNT photolysis in dioxane. As can be seen, a radical signal is observed almost immediately upon irradiation and quickly reaches a maximum value. The signal then decays slowly even with further irradiation, a non-radical species presumably being formed. When the ultraviolet lamp is extinguished, the signal changes abruptly. This indicates that the free radical production is a continuous process during irradiation and there is a rapid relaxation pathway in the absence of light, to undetermined radical and non-radical species. Relaxation predominately forms the non-radical species, since the signal in the

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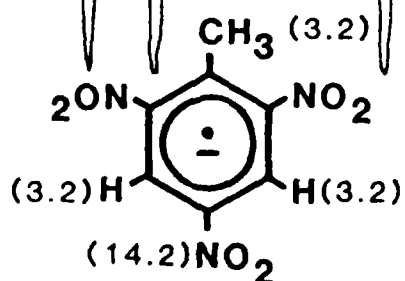
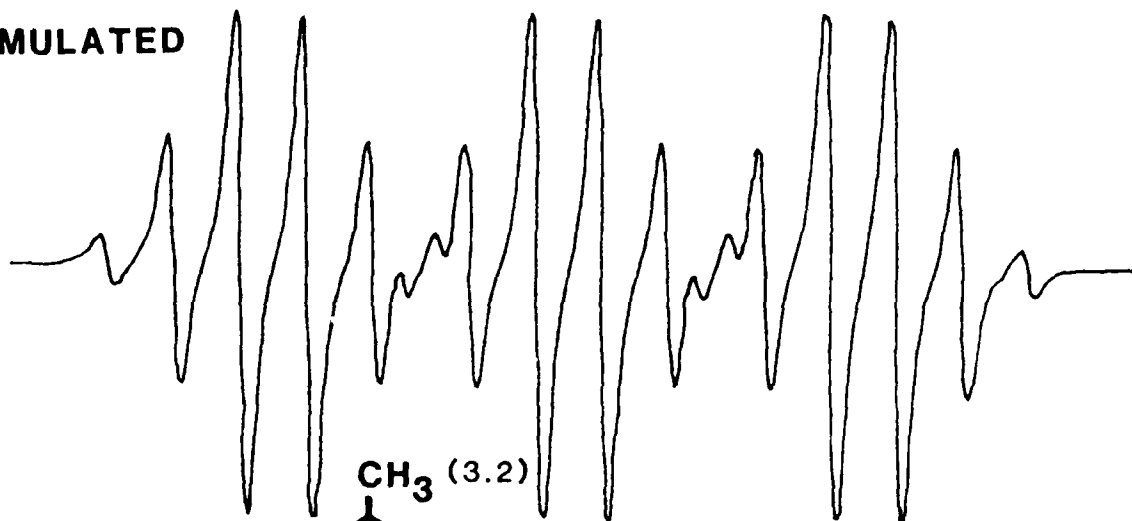
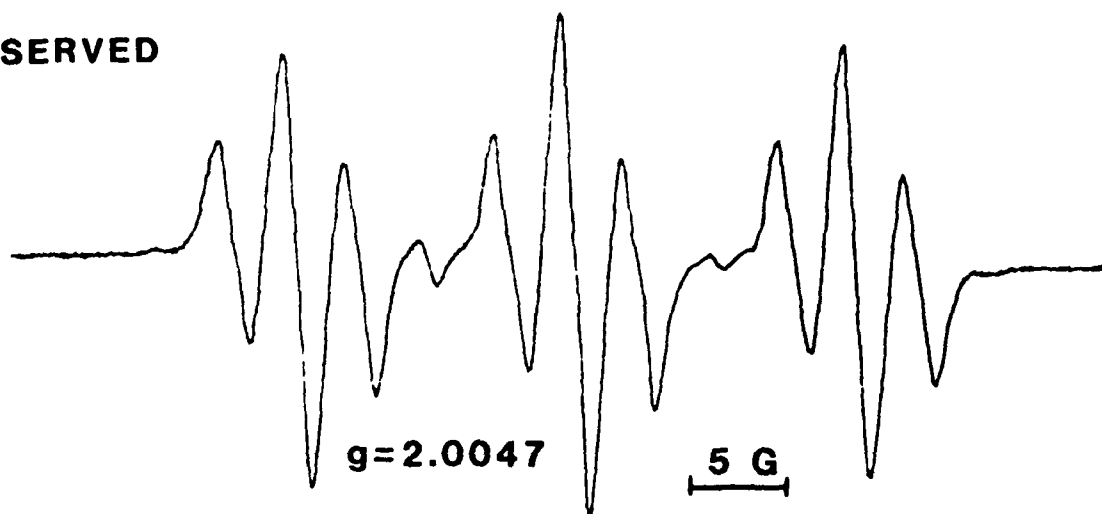


Figure 1. Observed and simulated EPR spectra of TNT in dioxane under ultraviolet irradiation. Experimental conditions: TNT concentration 0.1M, 100KHz field modulation frequency, 0.2G modulation amplitude, 8 mW microwave power, 1 minute full scan. Simulation performed using values of hyperfine splitting constants in Table 1.

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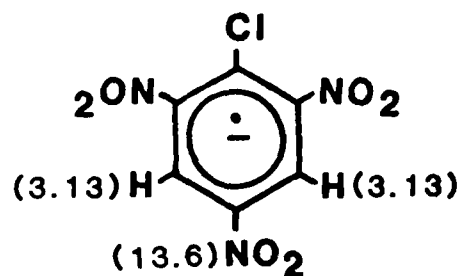
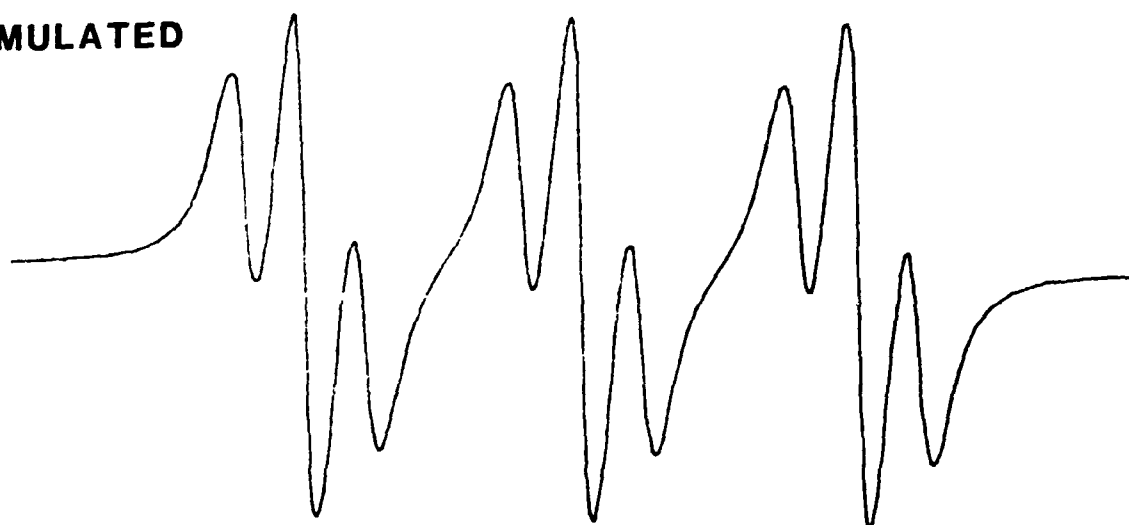
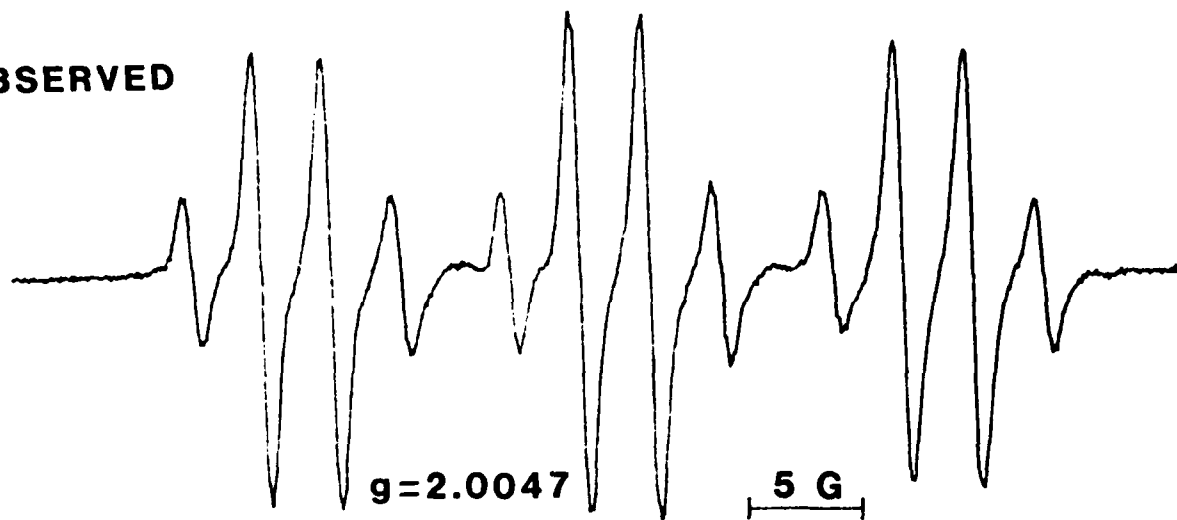


Figure 2. Observed and simulated EPR spectra of PiCl in dioxane under ultraviolet irradiation. Conditions as in Figure 1.

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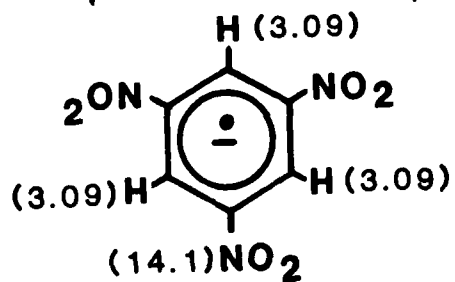
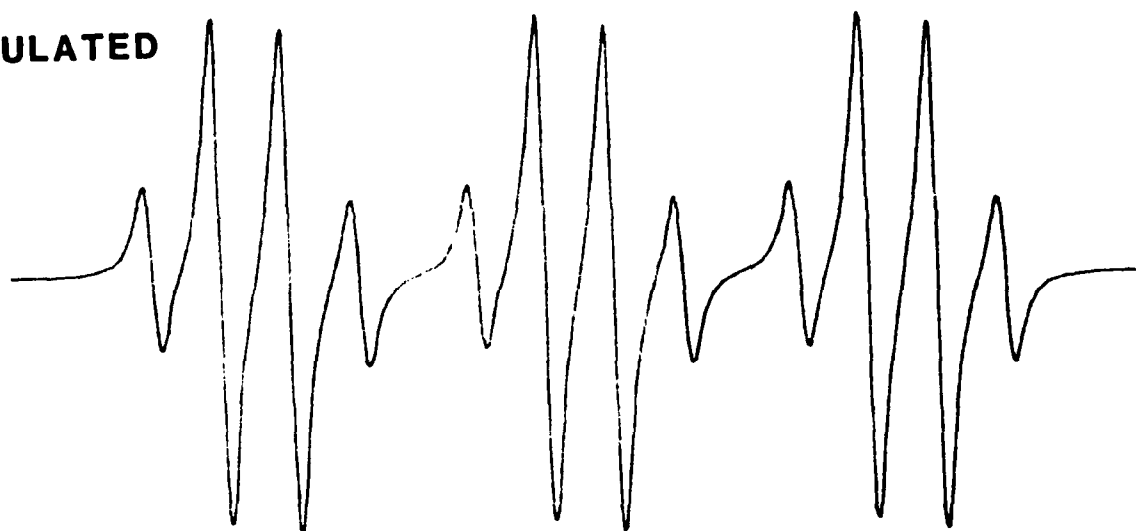


Figure 3. Observed and simulated EPR spectra of TNB in dioxane under ultraviolet irradiation. Conditions as in Figure 1.

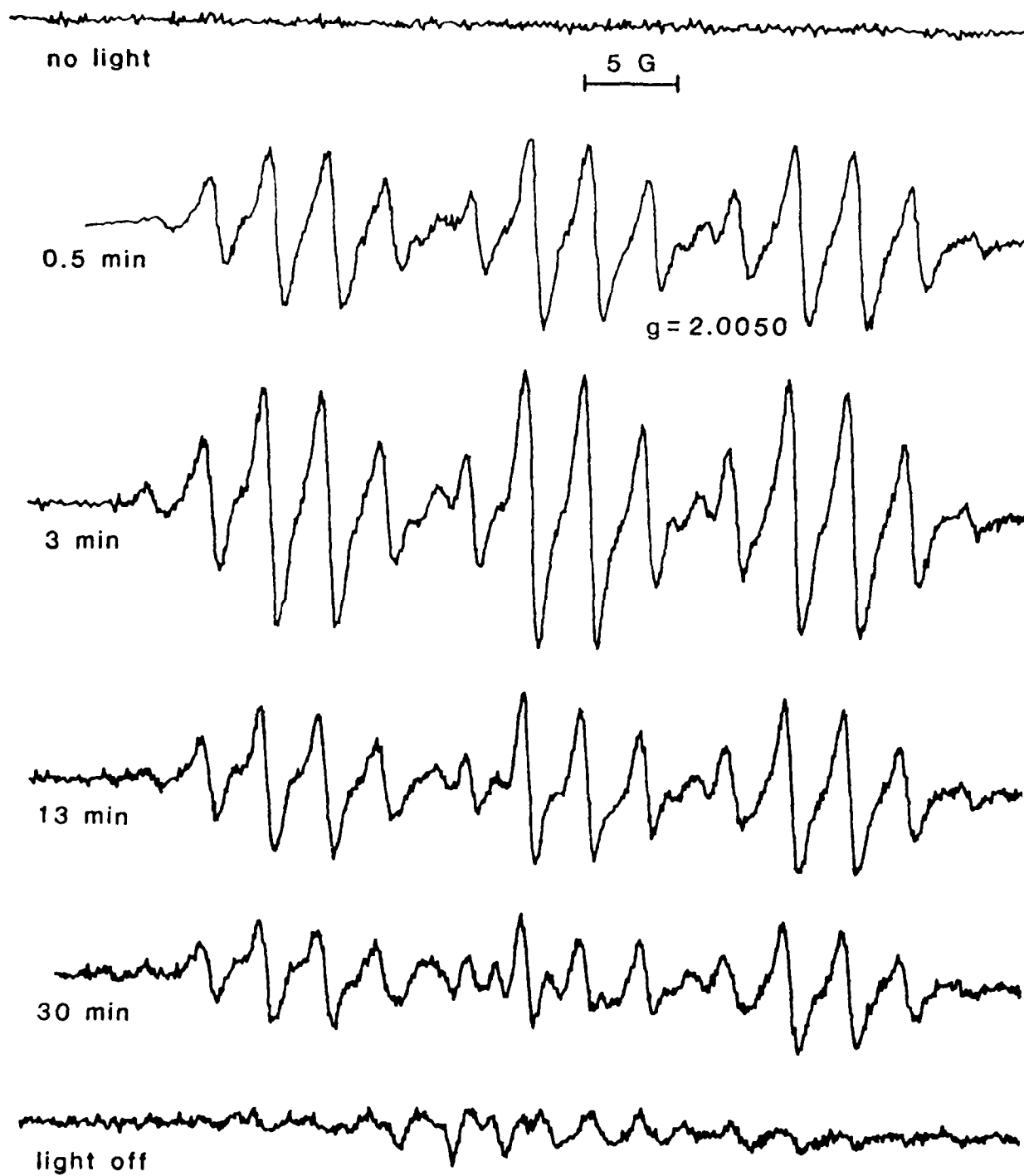


Figure 4. Time-dependent EPR spectra of TNT in dioxane under ultraviolet irradiation. Conditions as in Figure 1.

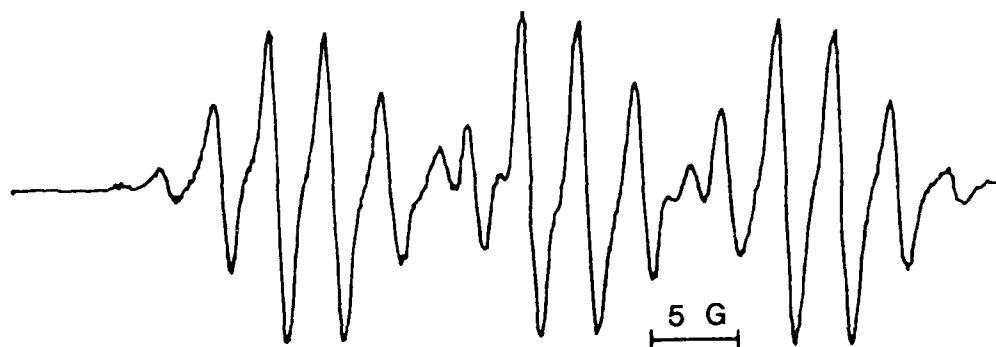
absence of light is weak. The solution, initially a very pale yellow, turns a strong orange during the experiment, as, in fact, happened with the majority of the nitroaromatics.

In contrast, the EPR spectrum of irradiated molten TNT (~ 80-100°C, too low a temperature for significant thermal decomposition to occur in our time frame) and TNT in acetonitrile show different hyperfine splitting patterns. In these, two equivalent nitrogen splittings are observed, leading us to believe that the nitro group para to the methyl group has been cleaved from the molecule. In this case, the free radical produced would be neutral. These spectra more closely approach the spectrum of TNT obtained during thermal decomposition as shown in Figure 5.

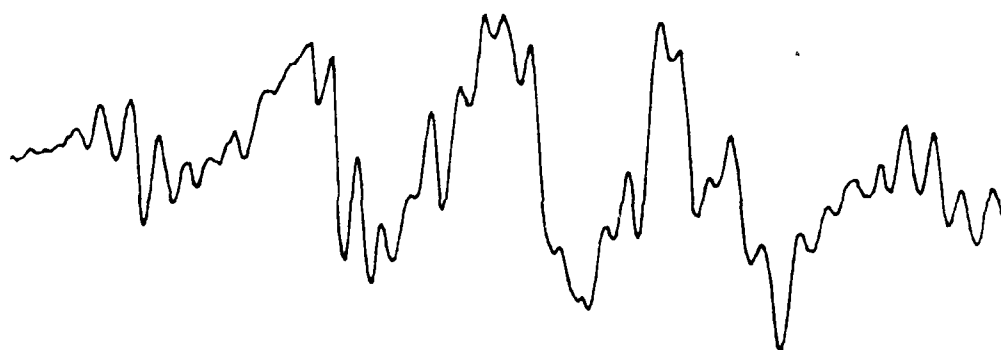
The second aspect of this phase of the project involved photolysis of the two nitramines RDX and HMX. Dioxane was again used as the primary solvent, even though the solubility of RDX and HMX was much lower than the majority of the nitroaromatics ( $\sim 10^{-5}$  M), which presented some sensitivity problems. However, here the dioxane appeared not to play a major role in free radical formation. The initial ( $\leq 2$  min) photochemical radical spectra of the nitramines resembled the early thermal radical spectra. Figure 6 shows the early spectra of both photochemically and thermally produced free radicals of HMX and RDX. The photochemical radicals can be simulated assuming loss of a nitro group, as shown in Figures 7 and 8. The low experimental sensitivity distorts the line heights somewhat, particularly in the case of RDX, but the identity of the two spectra is easily seen.

Again, upon long irradiation, the spectra change, but it is not a simple decay here. A second spectrum, much simpler, grows into the first. When the lamp is extinguished, again the first spectrum disappears, this

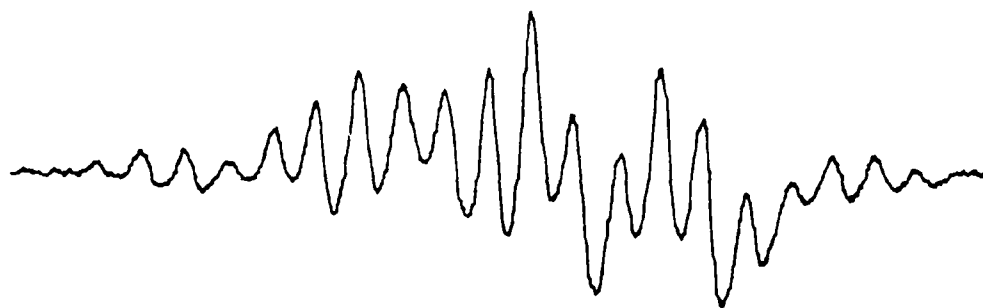




photolysis in dioxane



photolysis without solvent (molten)



thermal decomposition (molten)

Figure 5. EPR spectra of TNT under various conditions. Instrumental settings as in Figure 1. Temperature of TNT for thermal decomposition: 240°C.

photolysis of HMX

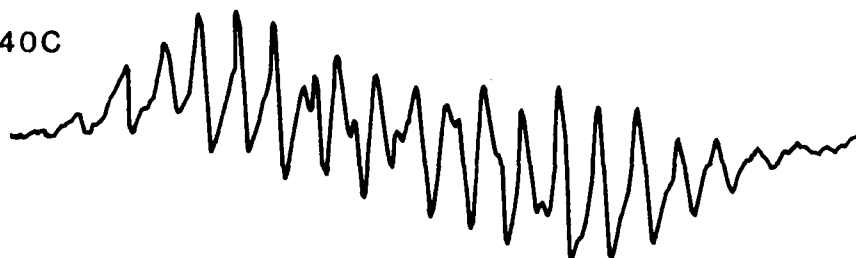
in dioxane



10 G

thermal decomposition

of HMX at 240C



photolysis of RDX

in dioxane



thermal decomposition

of RDX at 190C



Figure 6. Observed EPR spectra of the early HMX and RDX free radicals in dioxane (saturated) under ultraviolet irradiation and thermal decomposition without solvent. Instrumental conditions as in Figure 1.

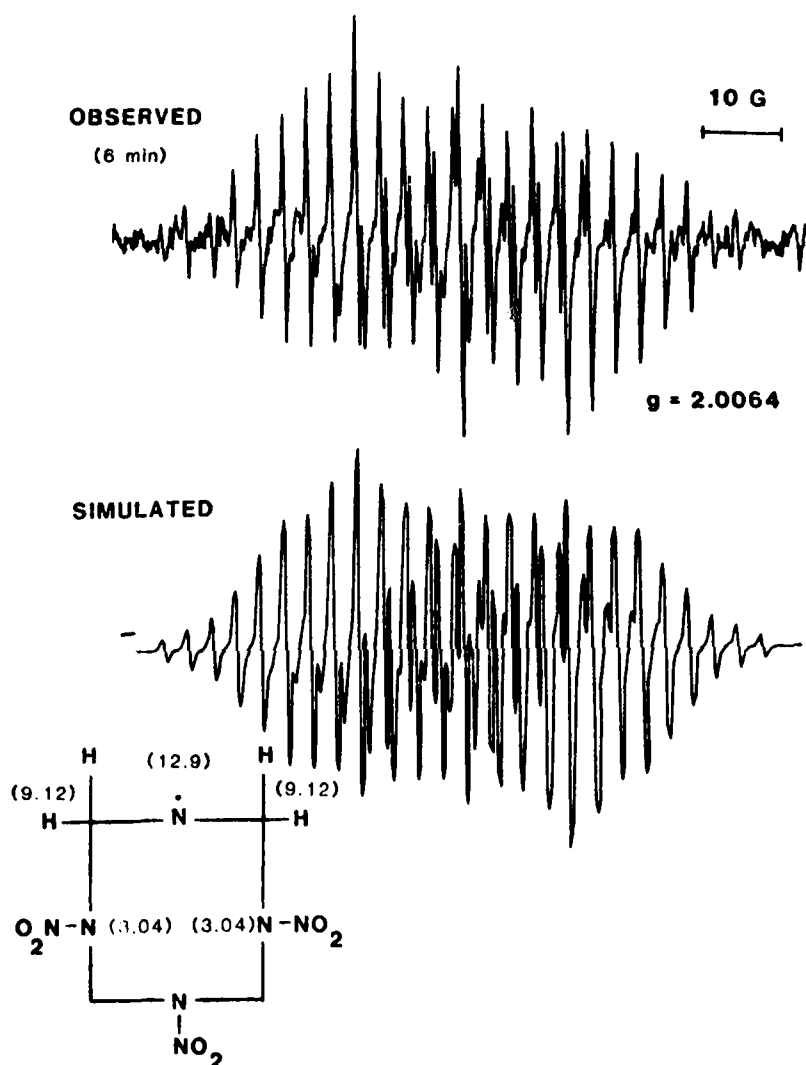


Figure 7. Observed and simulated EPR spectra of the early HMX radical under ultraviolet irradiation. Conditions as in Figure 1. Structure at bottom shows hyperfine splitting constants used in simulation.

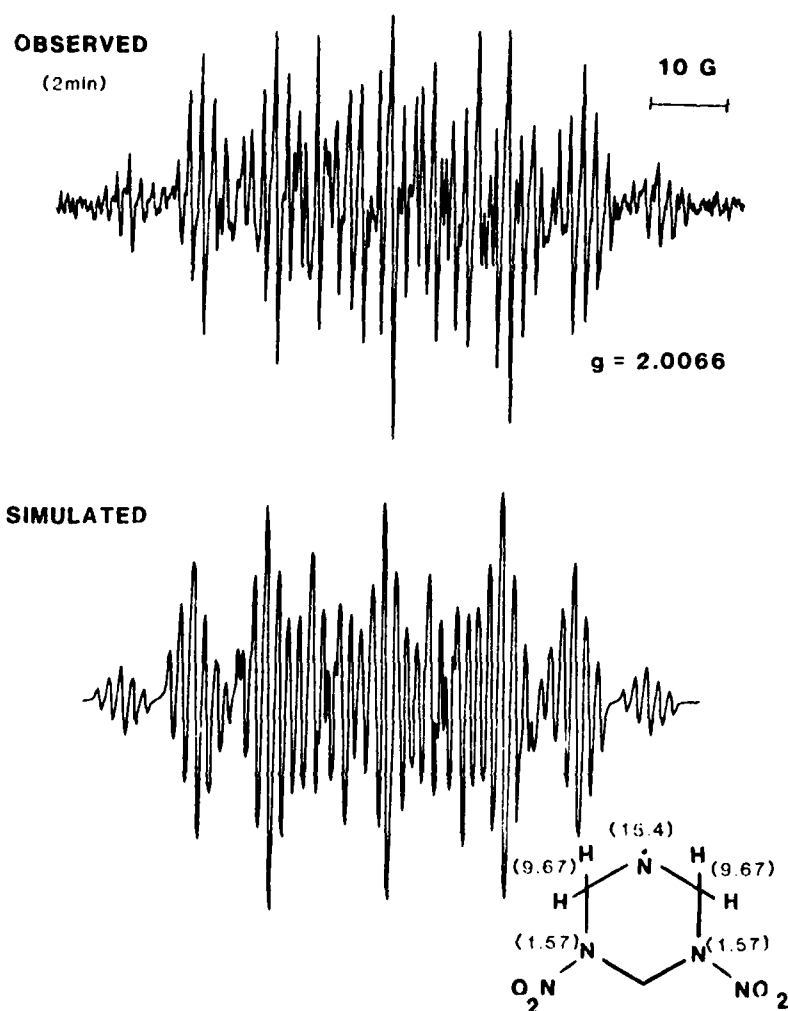


Figure 8. Observed and simulated EPR spectra of the early RDX radical under ultraviolet irradiation. Conditions as in Figure 7.

time leaving a persistent signal, almost as strong as the first radical. This signal appears to be due to a fragment of the original nitramine. In Figure 9, we show the late spectrum (dark) of HMX and a proposed structure of the radical with hyperfine splittings indicated. Figure 10 is the analogous spectrum of RDX and the splittings used in the simulation. No feasible structure for this radical has been proposed yet. No photochemical studies have been performed on molten HMX and RDX since these compounds melt at such high temperatures that thermal decomposition takes place.

#### Thermochemical Studies

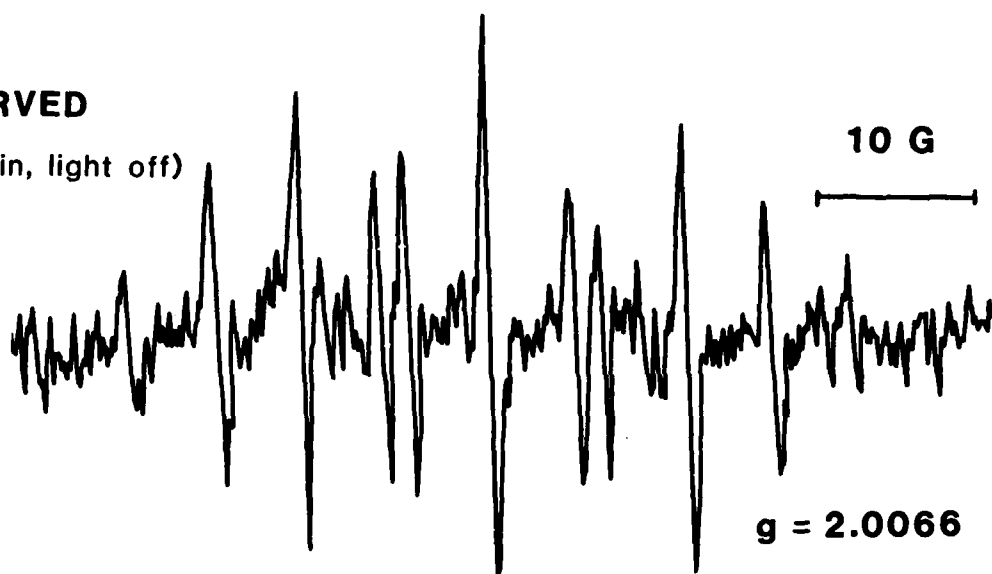
In August, the construction of our temperature controller was completed. At that time we began to study binary mixtures containing TNT to determine the molecularity of its thermal decomposition. "Convalex-10" a poly(phenyl ether), was first thought an appropriate candidate since it had no extractable hydrogen atoms, as did dioxane, was a liquid at room temperature, and was a fair solvent for TNT. Unfortunately, as TNT decomposed, it came out of solution. "Convalex-10" also appeared to promote the production of the polymeric radical species to the point that a broad single line masks the early structure of the spectrum (early spectrum shown in Figure 5). However, production of the early radical does appear to be slowed.

High-temperature silicone oil was also evaluated as a solvent. During decomposition, the TNT again separated from the solvent, and this substance was abandoned.

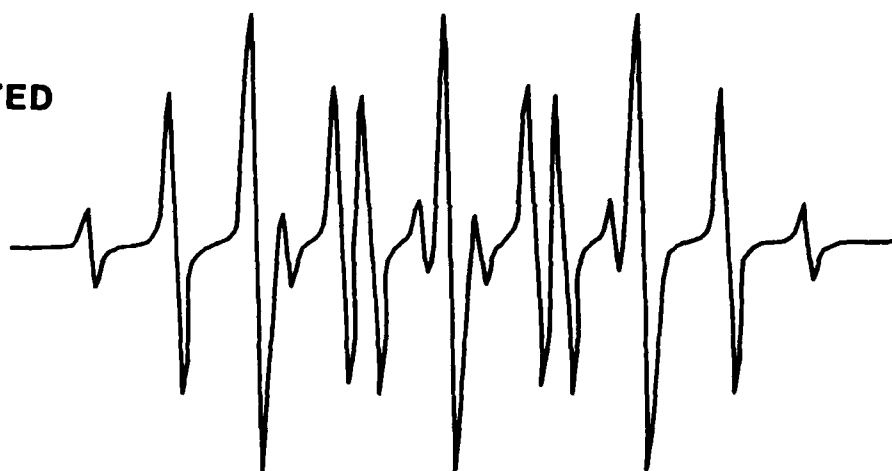
Finally, mixtures of TNT and TNB were studied. Radical production occurs at lower temperatures than in pure TNT (180 vs 230°C). This indicates that TNB is not an inert solvent at these temperatures, even though pure TNB does not produce radicals. However, the structure of the radical species obtained has not yet been identified.

**OBSERVED**

(35 min, light off)



**SIMULATED**



(12.2)

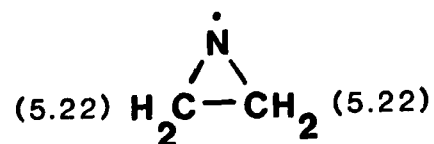


Figure 9. Observed and simulated EPR spectra of the late photolytic (lamp extinguished) HMX radical in dioxane (saturated). Conditions as in Figure 7.

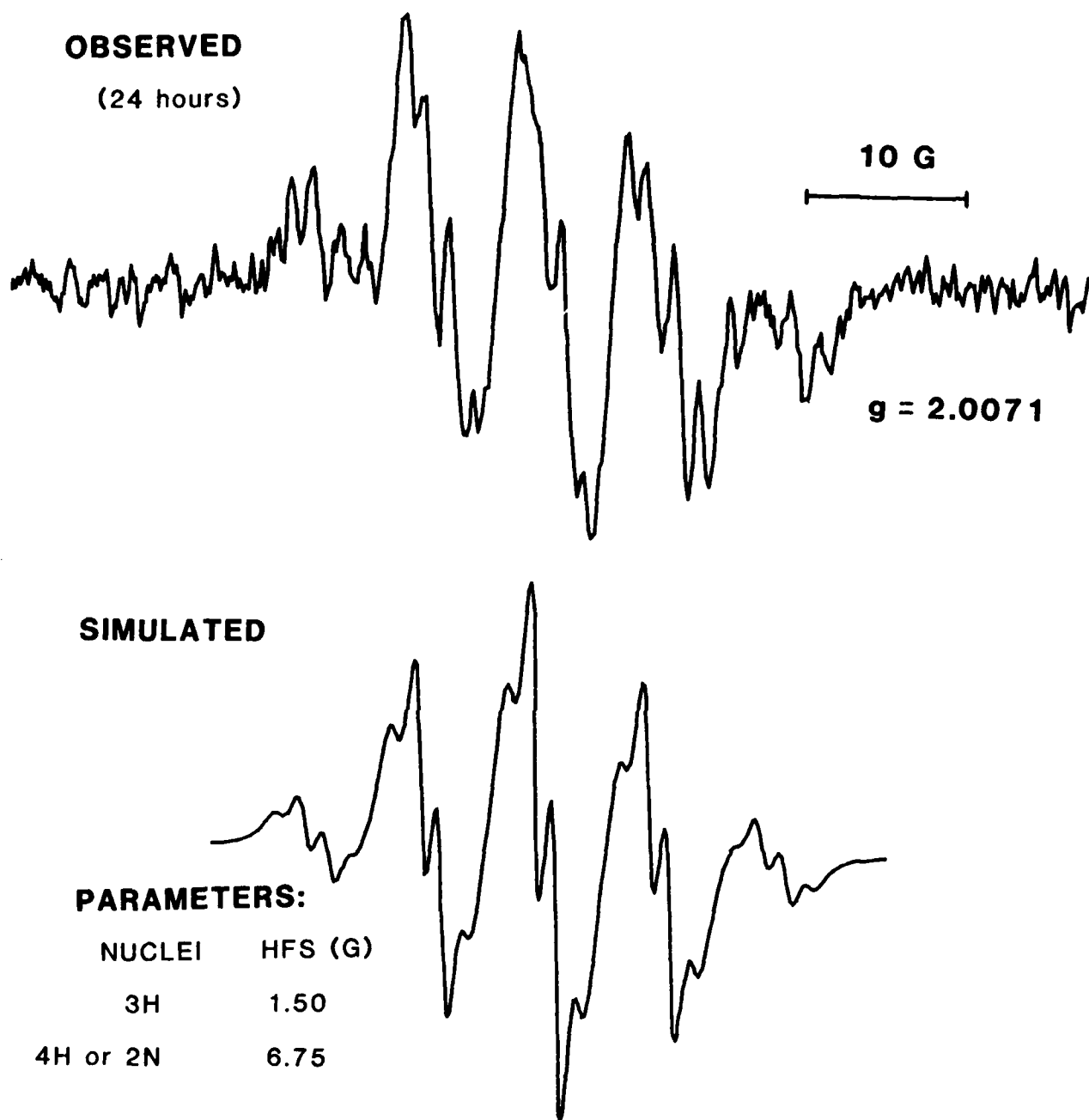
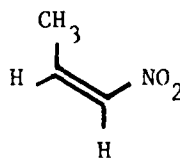
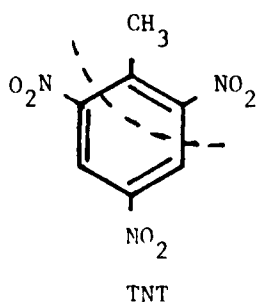


Figure 10. Observed and simulated EPR spectra of the late photolytic (lamp extinguished) RDX radical in dioxane (saturated). Conditions as in Figure 7. The structure of the radical has not been determined.

Computer calculations on thermal decomposition mechanisms have concentrated on the transfer of a hydrogen or oxygen atom between the methyl group of a TNT molecule and a nitro group of the same or a second molecule as the energetically difficult step. The four categories of this type of transfer are shown in Figure 11, and the calculated energy profile for one (intramolecular hydrogen transfer) is shown in Figure 12. The drawings at the top of the figure are three-dimensional computer representations of the molecule at various points along the reaction path.

We simulated the reaction pathway for a mechanism by defining a reaction coordinate (i.e., the distance between the transferring hydrogen and receiving oxygen in Figure 12), fixing that coordinate at points along the reaction path, and optimizing the entire molecular geometry at each of these points. The calculated heat of formation for each of these geometries was then used to determine a transition state and activation energy for the "reaction".

Since TNT is a large molecule, much computer time is required in order to calculate proposed reaction pathways. In order to shorten this time, we chose 1-nitropropene as a model system for TNT, since it is much smaller and has a backbone structurally similar to one end of a TNT molecule:



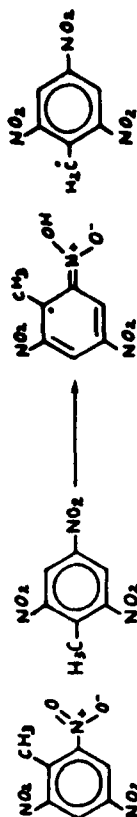
1-nitropropene



### INTRAMOLECULAR HYDROGEN TRANSFER



### INTERMOLECULAR HYDROGEN TRANSFER

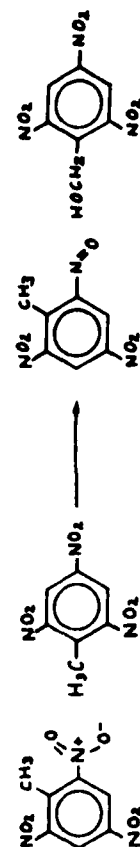


NOTE: TRANSFER ALSO POSSIBLE TO PARA-NITRO GROUP

### INTRAMOLECULAR OXYGEN INSERTION



### INTERMOLECULAR OXYGEN INSERTION



NOTE: INSERTION ALSO POSSIBLE FROM PARA-NITRO GROUP

Figure 11. Mechanisms for TNT thermal decomposition initial step currently being evaluated theoretically.

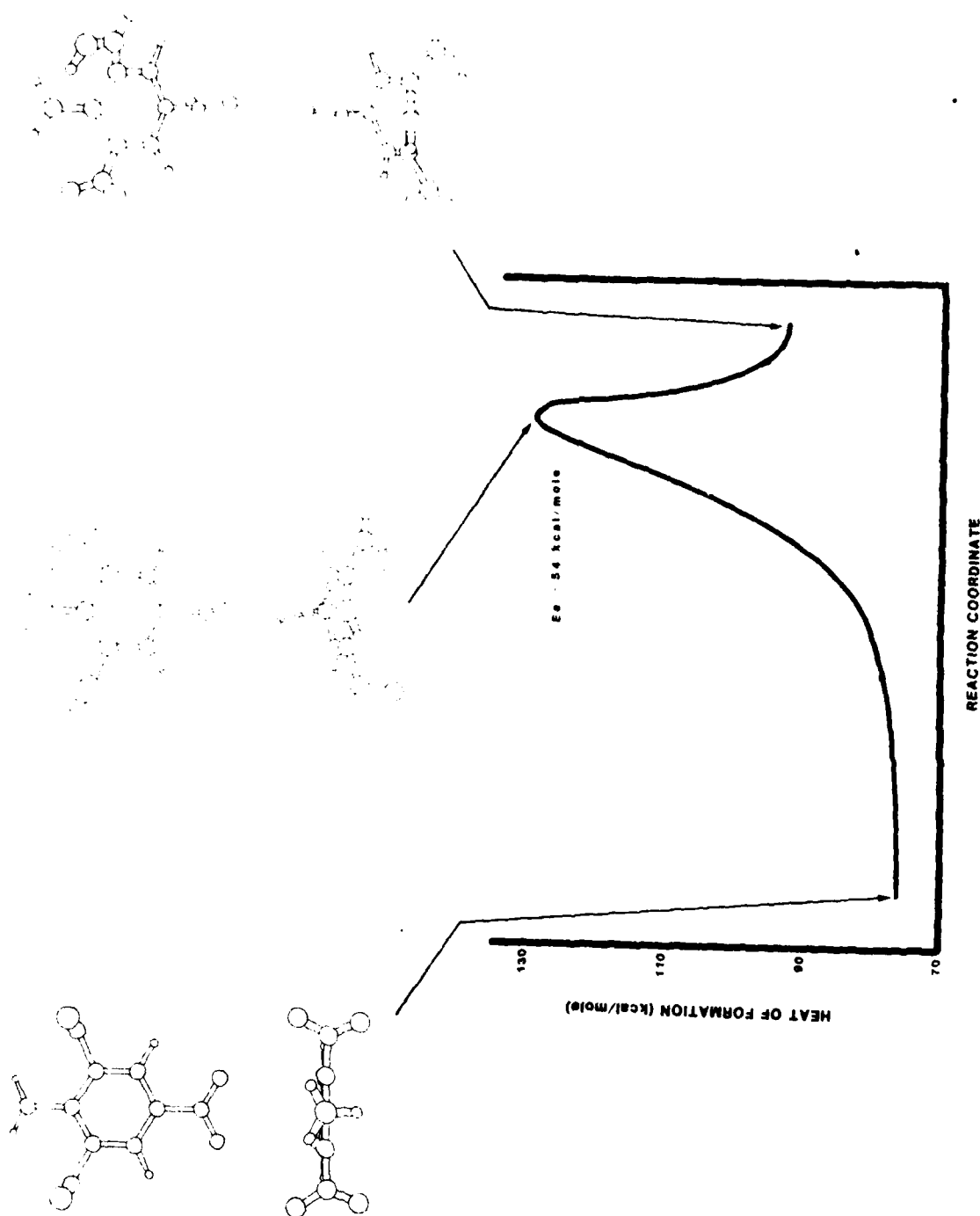
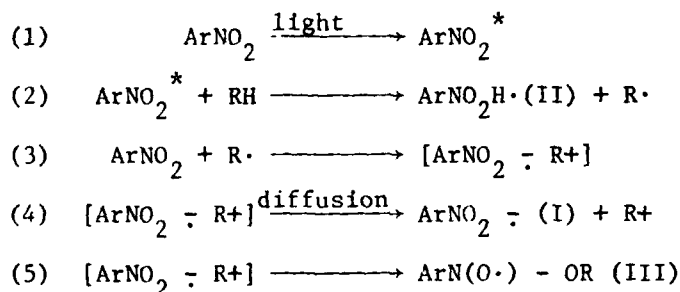


Figure 12. Theoretical energy diagram for intramolecular hydrogen transfer mechanism for TNT thermal decomposition. Drawings are three-dimensional representation of molecule at different stages of transfer.

Calculations using 1-nitropropene yield similar thermodynamic heats of reaction to products analogous to those in the four reaction schemes of TNT shown in Figure 11. For the TNT and 1-nitropropene calculations respectively, these are (in Kcal/mole): (1) Intramolecular H transfer: 16.6, 14.5; (2) Intramolecular O insertion: -49.9, -49.3; (3) Intermolecular H transfer: 16.8, 19.5; and (4) Intermolecular O insertion: -52.4, -48.5. Thus, 1-nitropropene shows promise as a model for TNT for these types of reactions. So far, the calculations on 1-nitropropene for intramolecular H transfer and O insertion have been completed, yielding an activation energy of 63.8 and 96 Kcal/mole respectively. The intermolecular mechanism calculations have not been completed at this time.

### Conclusions

Photochemical studies on nitroaromatic compounds in ethers indicated formation of three types of radicals: (I) the radical anion of the parent compound, (II) hydrogen atom addition to the parent compound, and (III) solvent adduct of the parent compound. This is consistent with a mechanism for photolysis of nitrobenzene and chloronitrobenzenes proposed by Cowley and Sutcliffe<sup>10,11</sup>:



Step (1) summarizes absorption by the nitroaromatic followed by intersystem crossing to the lowest triplet state  $T_1$ . The nature of  $T_1$  ( $n \rightarrow \pi^*$ ,  $\pi \rightarrow \pi^*$ ) has not been firmly established, although Baltrop and Bunce<sup>12</sup> have made an

argument for a  $\pi \rightarrow \pi^*$  state based on both experimental and theoretical evidence. We have performed CNDO/S calculations on nitrobenzene, and these results indicate that  $T_1$  for nitrobenzene is a  $\pi \rightarrow \pi^*$  state in agreement with Baltrop and Bunce. The excited triplet then abstracts a hydrogen atom from the solvent as shown in step (2). The radical formed (II) can be observed if it does not react rapidly. Its reactions have been discussed by Cowley and Sutcliffe<sup>10,11</sup>. Usually, however, subsequent steps (3) - (5) produce radical species very quickly whose spectra mask that of species II. The caged radical ion-pair produced in step (3) can either combine chemically to form the solvent-adduct (III) in step (5) or diffuse apart to produce the radical anion (I). The relative rates of these processes, thus which radical species will be observed, depend on solvent, temperature, and the nitroaromatic species itself.

In contrast photolysis of TNT in other acetonitrile and molten TNT produced radicals qualitatively similar to those found in thermal decomposition. A completely different structure of these radicals is indicated, namely the loss of a nitro group from the molecule. This is a feasible step in thermal decomposition, and supports findings of other workers of nitric oxide evolution.

In nitramine photolysis in ethers, the solvent appears to be inert. Products were again found to be consistent with those in thermal decomposition, with an initial loss of a nitro group. Later, different radicals appear, due to fragments of the original compound.

Thermochemical studies have not yielded any definitive results so far. An inert high temperature solvent for TNT has yet to be found. Thermal decomposition of TNT/TNB mixtures in particular indicate significant cooperation between the two molecules, but the nature of the interaction has not yet been determined.

### Plans for Future Study

Depending on the availability of a well controlled ultraviolet light source, kinetics studies of free radical production of both nitroaromatics and nitramines are feasible. Whether they are performed, however, depends on the progress of further thermal decomposition work, since photolysis is only a secondary to our project.

Detailed thermal decomposition studies via EPR are planned for the future. The main thrust for the near future will be on binary mixtures of TNT and nitramines with other compounds. The role of TNB as a solvent will continue to be studied, since it is often used in binary explosive formulations. Hexamethylbenzene seems promising as another high temperature solvent, since it melts at 164°C and boils much higher. Other possible compounds to be studied as solvents include high molecular weight hydrocarbons and high boiling esters. Plans are being made to collaborate with Dr. Larry Dalton of SUNY-Stony Brook on ENDOR and pulsed EPR experiments to separate species in time for a better understanding of the mechanism kinetically.

Theoretical calculations will be continued, both on mechanisms and possible radical structures. The exact nature of the calculations will depend on our experimental results.

# LIST OF ABBREVIATIONS

$d_2$ -TNBC- $\alpha$ -deuterated trinitrobenzyl chloride

$d_3$ -TNT- $\alpha$ -deuterated trinitrotoluene

DNB - dinitrobenzene

DNT - dinitrotoluene

HMX - cyclotetramethylene tetranitramine

NB - nitrobenzene

NT - nitrotoluene

PiCl - picryl chloride

RDX - cyclo-1,3,5-trimethylene-2,4,6-trinitramine

TCTNB - trichlorotrinitrobenzene

TNB - trinitrobenzene

TNBC - trinitrobenzyl chloride

TNT - trinitrotoluene

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